EFFECTS OF STOICHIOMETRY ON TRANSFORMATION TEMPERATURES AND ACTUATOR-TYPE PERFORMANCE OF NITIPD AND NITIPDX HIGH-TEMPERATURE SHAPE MEMORY ALLOYS

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ABSTRACT

Ternary NiTiPd and quaternary NiTiPdX (X=Au, Pt, Hf) high-temperature shape memory alloys (HTSMAs) were produced with titanium-equivalent (Ti+Hf) compositions from 50.5 to 49.0 at.%. Thermomechanical testing in compression was used to evaluate the transformation temperatures, transformation strain, work output, and permanent deformation behavior of each alloy to study the effects of quaternary alloying and stoichiometry on HTSMA behavior. Microstructural evaluation showed the presence of second phases for all alloy compositions. No-load transformation temperatures in the stoichiometric alloys were relatively unchanged by Au substitution, slightly increased by substitution with Pt, and severely depressed by substitution of Hf for Ti. Transformation temperatures were highest in the Ti-rich and stoichiometric compositions, and lower in the compositions with less than 50 at.% Ti (+Hf). During constant-load thermal cycling, transformation strain, and therefore work output, increased with increasing stress. Transformation strain was relatively unchanged by composition in the NiTiPdHf and NiTiPdPt alloys, while it decreased with decreasing Ti content in NiTiPd and increased with decreasing Ti content in the NiTiPdAu alloys. Permanent strain associated with the constant-load thermal cycling was lowest for alloys with Ti-equivalent-lean compositions. Based on these results, basic rules for optimizing the composition of NiTiPd alloys for actuator performance are discussed.

INTRODUCTION

Shape memory alloys have been receiving increased attention in the past decade as solid state actuator materials. Because of its low weight and high specific work output compared to hydraulic, pneumatic, and electrical motors and solenoids, nitinol (NiTi) has become the most common commercial shape memory alloy for actuator applications [1]. In binary NiTi, transformation temperature is controlled by composition with the highest temperatures occuring on the titanium-rich side of stoichiometry [2]. However, the maximum A_F transformation temperature for binary NiTi can only reach $\sim 100^{\circ}\text{C}$, and the martensite finish temperature $M_F \sim 70^{\circ}\text{C}$; therefore, actuator applications where a complete reset to martensite is required are limited to a maximum ambient use temperature generally less than 70°C [3].

Previous research over the years has shown that the transformation temperature of NiTi can be increased by alloying with Au, Hf, Pd, Pt, or Zr, where Au, Pd, and Pt substitute for Ni, and Hf and Zr substitute for Ti. Of these ternary alloys, NiTiPd has been studied the most. Research on NiTiPd alloys with palladium contents of 15, 20, 25, 30, and 46 at.% has shown that these alloys have high transformation temperatures, proportional to the Pd content, and good work output capability of over 9 J/cm³ [4,5]. However, all of the compositions were shown to exhibit poor dimensional stability, even at stress levels as low as 100 MPa. Further research showed that alloying of Ni_{19.5}Ti_{50.5}Pd₃₀ by substituting 5 at.% Au or Pt for 5 at.% Pd can improve dimensional stability without affecting the transformation temperature, but still not to a level acceptable for long term thermal cycling in an actuator application [4,5].

One of the reasons for the poor dimensional stability in the high-temperature NiTiPd alloys studied [4,5] may be that they were all produced with slightly titanium rich compositions. Like binary NiTi, the transformation temperatures in ternary NiTiPd alloys are very sensitive to changes in the equivalent Ni:Ti ratio [3,6-8]. For a 1 at.% drop in composition below 50.0at% Ti, the transformation temperature can drop by over 100°C [2]. Therefore, the NiTiPd, NiTiPdAu, and NiTiPdPt alloys in ref. [4,5] were made with target Ti contents of 50.5 at.% to maintain high transformation temperatures. However, research performed by Morgan on nickel rich and titanium rich compositions of NiTi has shown that the dimensional stability of binary titanium rich alloys is very poor compared to that of nickel rich alloys [9]. In the present work, research was performed to determine if the same link between equivalent Ni:Ti ratios and dimensional stability existed in the NiTiPd alloys, and if quaternary substitutions could improve upon the transformation temperatures, transformation strain, work output, and dimensional stability of NiTiPdX HTSMAs for their potential use as actuator materials.

MATERIALS PROCESSING AND CHARACTERIZATION

Material Processing

Four different series of alloys were produced: Ni_{70-X}Ti_XPd₃₀, Ni_{70-X}Ti_XPd₂₅Au₅, Ni_{70-X}Ti_XPd₂₅Pt₅, and Ni_{70-X}Ti_{X-3}Pd₃₀Hf₃. For each alloy series, the nickel and titanium contents were varied to produce titanium-equivalent (Ti+Hf) compositions of 50.5, 50.0, 49.5, and 49.0 at.%. The sixteen resulting target compositions were fabricated as small 30g melts by arc melting of high purity elemental constituents (99.98 Ni, 99.95 Ti, 99.995 Pd, 99.995 Pt, 99.995 Au, 99.5 Hf). The arc melting was performed under a high purity argon atmosphere by melting the constituents in a water cooled copper crucible using a non-consumable tungsten electrode. To ensure complete mixing of the elements, which have widely varying densities, the buttons were inverted and remelted 3 times. The final buttons were vacuum homogenized at 900°C for 72 hours. Using a wire EDM, cylindrical rods of just over 5mm diameter were cut from the homogenized buttons. These rods were centerless ground to 5mm diameter and then sliced by wire EDM into 10mm lengths for subsequent compression testing.

Microstructural Characterization

For microstructural analysis, samples were cut by EDM from the buttons, mounted in Bakelite, and polished. The surfaces were subjected to a five step grind/polish regimen

and then finished off with a mild attack polish [4]. The microstructures of the materials were then studied in the as-polished condition using a JEOL 840 SEM and Hitachi 4700 FE-SEM, with phases being qualitatively determined using EDS.

Mechanical Test Equipment

Sample testing was performed on an MTS 810 servo-hydraulic load frame with an MTS FlexTest multi-channel digital controller. Sample temperature was measured using one type K thermocouple spot welded directly to the middle of the sample gage section. Temperature was controlled by inductively heating the hot grip ends near the sample using water cooled copper coils driven by an Ameritherm induction furnace. Heating rates were controlled at 30°C/min and cooling rates kept to a maximum of 30°C/min. Samples were strained at a constant rate of $1 \times 10^{-4} \, \text{sec}^{-1}$, while strain was measured by a non-contact Opto2600 LED extensometer. Stress was calculated (and used as a control channel) from input gage diameter and force measured from the MTS 100kN load cell.

Thermomechanical Testing Procedures

Constant stress thermal cycles were performed in compression by loading the 10mm x 5mm dia, sample in the low temp martensite phase at 1x10⁻⁴ sec⁻¹ until a pre-determined axial stress was reached. Stress was held constant while the sample was heated from the low temperature martensite state through the transformation to the high temperature austenite state and then cooled to the initial temperature. The samples were loaded in successive steps of 2, 100, 200, and 300 MPa. The first stress level is referred to as "noload" but a stress of 2 MPa had to be applied to prevent jitter and loss of contact between the sample and platens, which would have given erroneous strain values. At each stress level, the sample was subjected to two heat-cool thermal cycles – the first cycle to allow the material to "reset" at that stress, and the second to measure behavior at that stress. During each heat-cool cycle, the strain change in the gage was measured as a function of temperature. From the second cycle strain-temperature data, the transformation temperatures, transformation strain, and open loop strain were measured with respect to the applied stress (Fig. 1). Transformation strain was measured as the strain difference between the beginning and end of the martensite to austenite transformation upon heating. Work was calculated as the integral of the applied stress with respect to this change in strain, which for a constant stress situation, simplifies to the applied stress times the transformation strain. The strain level difference in the martensite before and after the second heat-cool thermal cycle, or "open loop strain", is a measure of dimensional stability. For a perfectly dimensionally stable material, the difference in strain will be zero – the strain in the martensite at a given temperature will be exactly the same cycle after cycle.

RESULTS AND DISCUSSION

Material Characterization

The microstructures of all the cast alloys after homogenization were very similar and exhibited a martensitic matrix and a major second phase. Representative micrographs showing the microstructure of the 49.5 at.% Ti(+Hf) are shown in Fig. 2(a-d). The second phase was identified as the cubic (Ti,Hf)₂(Ni,PdX) phase which is similar to the

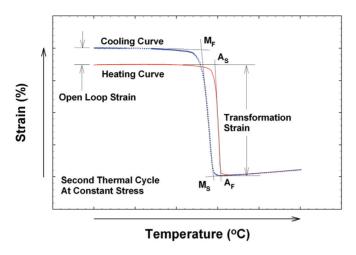


Figure 1: Method of measuring properties from a constant stress thermal cycle.

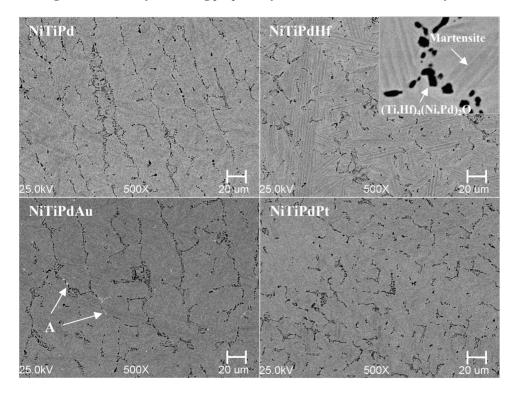


Figure 2: Microstructure of samples with 49.5 at.% titanium-equivalent compositions.

cubic Ti_2Ni phase reported in the binary NiTi alloys. There was a small amount of TiO_2 also present in all alloys and an occasional Au rich phase in the NiTiPdAu alloys (marked A in Fig. 2(c)). The Ti_2Ni -type phase has been shown to be stabilized by oxygen and is actually a $Ti_4Ni_2O_Y$ type phase. According to Zhang *et al*, even the low partial pressure of oxygen present in a high purity argon atmosphere with a titanium getter at $1000^{\circ}C$ is enough to oxidize a binary NiTi sample and form TiO_2 and $Ti_4Ni_2O_Y$

[11]. As the samples studied here were melted only under a partial pressure high purity argon atmosphere, the major second phase present in our alloys is likely due to oxygen contamination of the melt and is oxygen stabilized (Ti,Hf)₄(Ni,Pd,X)₂O_Y phase.

Transformation Temperature

Transformation temperatures were determined for each composition during "no-load" (actually 2MPa) constant stress thermal cycling (Fig 3). In the ternary Ni_{70.x}Ti_xPd₃₀ series, the 30 at.% Pd content raised the M_F temperature (the lowest transformation temperature data for each series of alloy) in the titanium-rich composition up to 248°C. an increase of 178°C over the maximum seen in binary NiTi alloys. However, some of this improvement in transformation temperature was lost when the Ti content was reduced below 50 at.%, dropping the M_F transformation temperature to 157°C at 49 at.% Ti. The substitution of 5 at.% Pt for Pd raised the transformation temperatures by an average of 18°C for the compositions studied – most strongly in the stoichiometric and 49.5 at.% Ti materials. The NiTiPdAu samples had transformation temperatures that were on average 14°C lower than those in the ternary alloy. The substitution of 3 at.% Hf for Ti had the strongest effect of the three quaternary elements, dropping the no load transformation temperatures by an average of 94°C, with the greatest difference in the 50.5 at.% and 49.0 at.% Ti+Hf samples. All of the quaternary alloys exhibited a strong drop in transformation temperatures as a function of decreasing Ti+Hf content, with the highest transformation temperatures in the stoichiometric or Ti+Hf rich compositions. For all alloys and compositions, M_S, A_S, and A_F followed the same trends as the M_F temperature. For each alloy series, the transformation temperatures from lowest to highest temperature were M_F , A_S , M_S , and A_F .

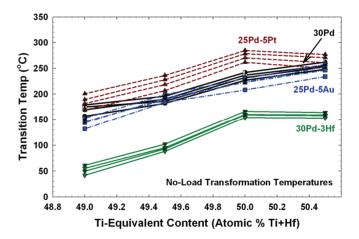


Figure 3: Transformation temperatures for the four series of alloys determined through constant "no-load" (2 MPa) thermal cycling.

Transformation Strain and Work Output

Transformation strains were evaluated at constant stresses of 100, 200, and 300 MPa. However, for clarity, only the transformation strains at 200 MPa are shown here (Fig. 4). In the ternary NiTiPd alloys, transformation strains were highest in the stoichiometric composition, slightly reduced in the 50.5 and 49.5 at.% Ti compositions,

and lowest at 49.0 at.% Ti. The Pt and Hf alloyed materials have transformation strains with no clear trends as a function of equivalent Ti content, but which remain in a relatively constant range between 3.28 and 3.65% in the Pt alloyed material, and between 3.31 and 3.82% in the Hf alloyed material. Alloying with Au results in transformation strains which are lowest in the Ti-rich composition, at 2.70%, but increase with decreasing Ti content to 4.26% at 49.0 at.% Ti.

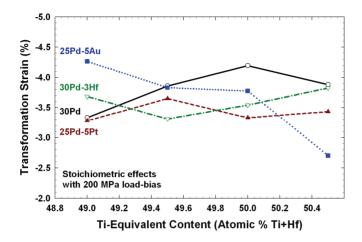


Figure 4: Transformation strain as a function of Ti-equivalent content for all compositions evaluated at 200 MPa.

Work output is calculated by multiplying the applied stress by the transformation strain, effectively scaling the values. Thus, the same trends seen in the transformation strain are observed in the work output (Fig. 5). In the NiTiPd alloy series, the maximum work output, 8.39 J/cm³, is seen in the stoichiometric composition, while the minimum work output, 6.67 J/cm³, occurs in the composition with 49.0 at.% Ti. The work output for the Pt and Hf alloyed materials remains in a constant band with composition. The Au alloyed material exhibits work output that increases with decreasing Ti content, from 5.40 to 8.53 J/cm³ between 50.5 and 49.0 at.% Ti, respectively.

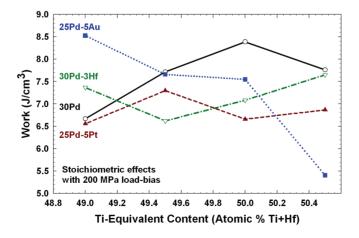


Figure 5: Work output as a function of Ti-equivalent composition at 200 MPa load-bias.

Dimensional Stability

One of the major issues with high temperature NiTiPd alloys is poor dimensional stability during load-biased thermal cycling [4.5]. The current data is consistent with these prior studies, with the ternary NiTiPd alloys exhibiting extensive open loops, or irrecoverable strains during thermal cycling at 200 MPa (Fig. 6), as well as 100 and 300 MPa. However, open loop strain in the ternary alloy decreased with decreasing Ti content from 0.47% at 50.5 at.% Ti to 0.32% in the 49.0 at.% Ti composition. There was a negligible change in behavior in the Pt alloved compositions, with 0.48% and 0.31% open loop strain at 50.5 and 49.0 at.% Ti respectively. Alloying with Au decreased the open loop strain by an average of 0.11% to 0.33% and 0.23% in the 50.5 and 49.0 at.% Ti compositions, respectively. The strongest effect on dimensional stability came from the 3 at.% Hf substitution for Ti, especially considering that the substitution was only for 3 at.% Hf. while the Au and Pt were substituted at 5 at.%. In the NiTiPdHf alloy series, the open loop strain was reduced by an average strain of 0.21% from that of the NiTiPd alloy series, to 0.23% and 0.18% in the 50.5 and 49.0 at% Ti compositions, respectively. All four alloys exhibited open loop strains that were highest in the stoichiometric or Ti-rich compositions and lowest in the 49.0 at.% composition, as was anticipated based on prior research on binary NiTi alloys [9].

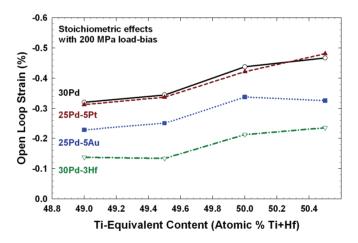


Figure 6: Single-cycle open loop strain as a function of Ti-equivalent content.

Optimization of Properties

As the end use of these materials is for solid state actuators, it is necessary to be able to determine the optimum composition which would give the properties desired for a specific application. For an actuator application with low cycle count, where high transformation temperature is more important than dimensional stability, the optimum material would be a stoichiometric or Ti-rich NiTiPd alloy, which would combine high transformation temperatures (Fig. 7) with high transformation strain (Fig. 8). For this application, a stoichiometric NiTiPdAu or NiTiPdPt composition would also be good, with high transformation temperatures, moderate transformation strains, and improved dimensional stability. However, for long term high cycle actuator applications where transformation temperature is less important than dimensional stability, the optimum material would be a Ti-equivalent lean NiTiPdAu or NiTiPdHf composition, combining

good dimensional stability with moderate to high transformation strain. In the end however, additional research needs to be performed to further improve the dimensional stability of NiTiPd-based high-temperature shape memory alloys, preferably without impacting the transformation temperatures.

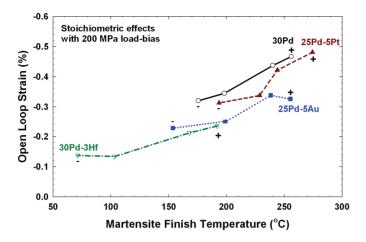


Figure 7: Open loop strain as a function of the no-load M_F temperature. The (+) and (-) in the figure denote the respective Ti-equivalent rich and Ti-equivalent lean compositions of each alloy system. The linear trend seen here is not due to thermal effects, as the samples were all cycled to the same upper temperature regardless of transformation temperature.

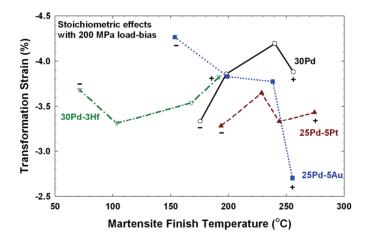


Figure 8: Transformation strain as a function of the no-load M_F temperature. The (+) and (-) in the figure denote the respective Ti-equivalent rich and Ti-equivalent lean compositions of each alloy system.

SUMMARY AND CONCLUSION

All sixteen compositions studied were composed of a martensitic matrix with secondary (Ti,Hf)₄(Ni,Pd,X)₂O_X phase present. Transformation temperatures were highest in Ti-

equivalent rich compositions, and decreased with decreasing Ti content. The highest transformation temperatures were observed in the NiTiPdPt alloy series, were lower in the NiTiPd and NiTiPdAu alloys, and severely reduced in the NiTiPdHf series. Transformation strain and work output behaviors were different for all four alloys, with transformation strain decreasing with decreasing Ti content for NiTiPd, increasing with decreasing Ti content for NiTiPdAu, and remaining relatively constant for different compositions in NiTiPdHf and NiTiPdPt. Open loop strain was highest in the NiTiPd and NiTiPdPt alloys, reduced in the NiTiPdAu alloy, and lowest in the NiTiPdHf alloy.

By plotting the measured open-loop strain and transformation strain as a function of the no-load martensite finish temperature, the optimum compositions for a particular application can be selected. If stability is not an issue, Ti-rich or stoichiometric alloys are better for actuator applications requiring high transformation strains. If dimensional stability is an issue, quaternary NiTiPdX alloys are better, with Hf showing greater benefit as an alloying element than Au or Pt, and at lower levels (3 at.% compared to 5 at.%), but with lower transformation temperatures. However, transformation temperatures could possibly be improved by reducing the level of Hf in the alloys.

ACKNOWLEDGEMENTS

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Effects of Stoichiometry on Transformation Temperatures and Actuator-Type Performance of NiTiPd and NiTiPdX High-Temperature Shape Memory Alloys

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High-temperature shape memory NiTiPd and NiTiPdX (X=Au, Pt, Hf) alloys were produced with titanium equivalent (Ti+Hf) compositions of 50.5, 50.0, 49.5, and 49.0 at.%. Thermo-mechanical testing in compression was used to evaluate the transformation temperatures, transformation strain, work output, and permanent deformation behavior of each alloy to study the effects of quaternary alloying and stoichiometry on hightemperature shape memory alloy behavior. Microstructural evaluation showed the presence of second phases for all alloy compositions. No load transformation temperatures in the stoichiometric alloys were relatively unchanged by Au and Pt substitutions, while the substitution of Hf for Ti causes a drop in transformation temperatures. The NiTiPd, NiTiPdAu and NiTiPdHf alloys exhibited transformation temperatures that were highest in the Ti-rich compositions, slightly lower at stoichiometry, and significantly reduced when the Ti equivalent composition was less than 50 at.%. For the NiTiPdPt alloy, transformation temperatures were highest for the Ti-rich compositions, lowest at stoichiometry, and slightly higher in the Ni-rich composition. When thermally cycled under constant stresses of up to 300 MPa, all of the alloys had transformation strains, and therefore work outputs, which increased with increasing stress. In each series of alloys, the transformation strain and thus work output was highest for stoichiometric or Ti-rich compositions while permanent strain associated with the constant-load thermal cycling was lowest for alloys with Ni-equivalent-rich compositions. Based on these results, basic rules for optimizing the composition of NiTiPd alloys for actuator performance will be discussed. (This work was funded by the NASA Fundamental Aeronautics Program, Subsonic Fixed Wing Project.)

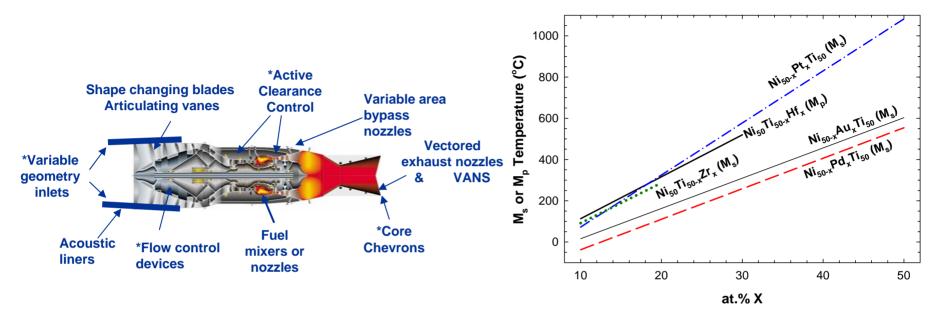


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Goal and Direction of Research

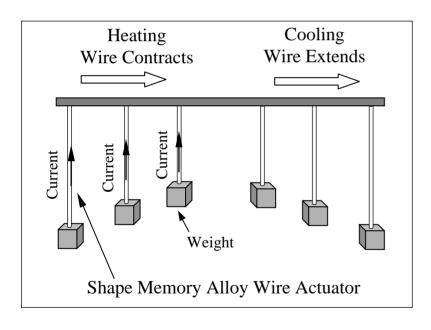


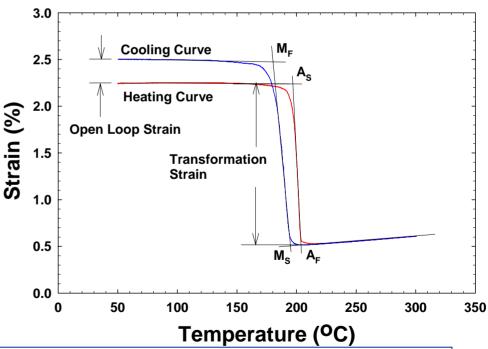
- HTSMAs are being developed with goal of being used for active structures in aircraft engines
 - Quieter engines, improved efficiency, versatility
- These systems operate at high temperature
- High transformation temperature known for almost 30 years
- Very limited research on ∫σ dε (work) mostly SME

Introduction: Shape-Memory & Work



- Shape Memory Effect shape change associated with a recoverable phase transformation between low temperature Martensite and high temperature Austenite
- Work (∫σ dε) shape change against a bias-load

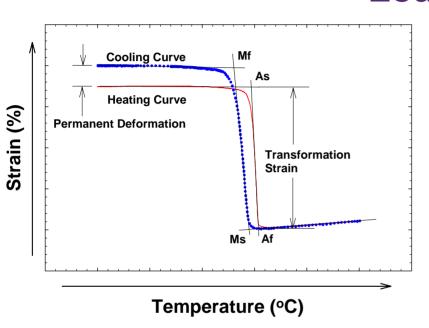


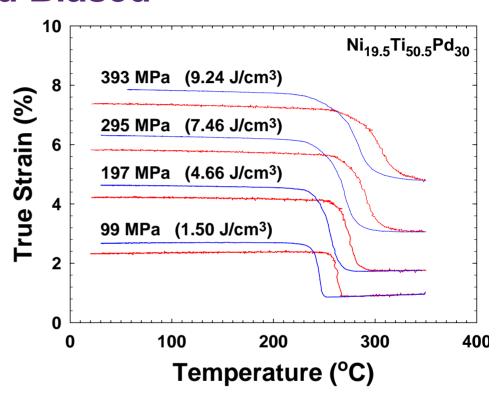


At 4 J/cm³ a 44 mil wire 25" long is capable of lifting 44 lbf 0.5"

Actuator Mimicking Tests: Thermal Cycling Under Constant Load "Load Biased"







1. Measured Properties

- a) Transformation Temperatures: Mf, Ms, As, Af
- b) Transformation Strain
- c) Permanent Deformation

2. Calculated Properties

a) Specific Work Output

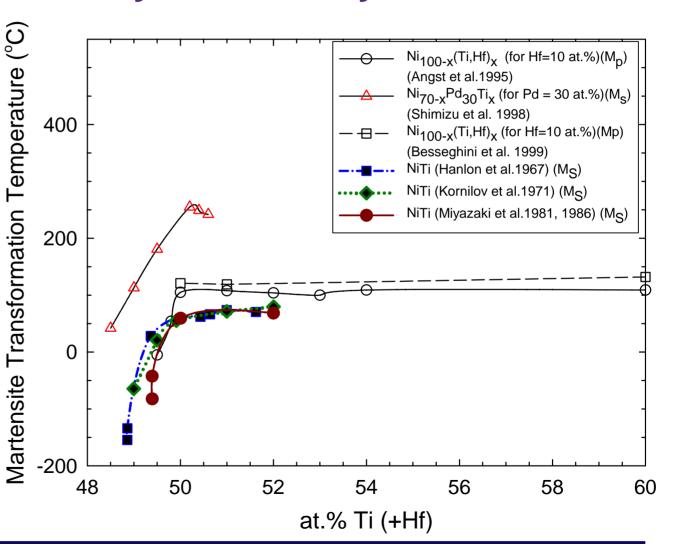
Work =
$$\int \sigma d\epsilon = \sigma \cdot \epsilon$$

Stoichiometry and Transformation Temperatures



- Binary and Ternary-

compositions to be titanium-rich because transformation temperatures drops off on titanium-lean side



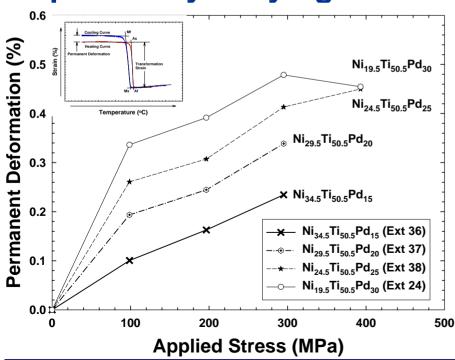
High Temperature SMAs Titanium-rich Ternary and Quaternary

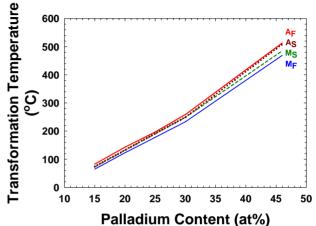


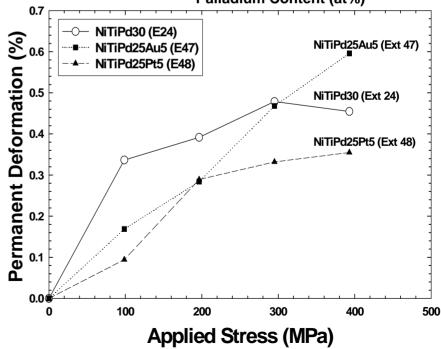
 Ternary alloying with Pd raises transformation temps

 Ternary Ti-rich NiTiPd show high levels of permanent strain

 Can be improved somewhat by quaternary alloying





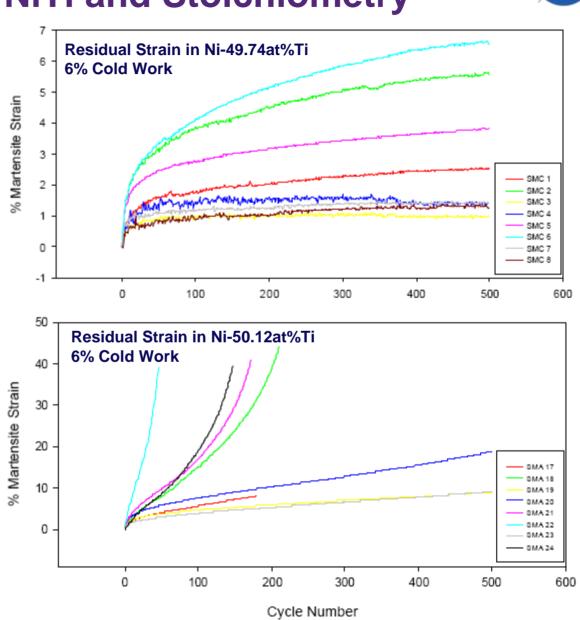


Binary NiTi and Stoichiometry

NASA

- Permanent deformation extreme in Ti-rich binary alloys
- Best performing
 Ti-rich here is only
 as good as the
 worst performing
 Ti-lean

Ref. - N. Morgan, "The Stability of NiTi shape memory alloys and actuator applications," Doctoral Thesis. Cranfield University, Swindon. Wiltshire, UK (1999)



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Objective of Study

- Re-examine ternary NiTiPd and quaternary NiTiPdX alloys to determine effect of stoichiometry on:
 - Transformation temperatures
 - Transformation strain & work output
 - Dimensional stability (Open loop strain)

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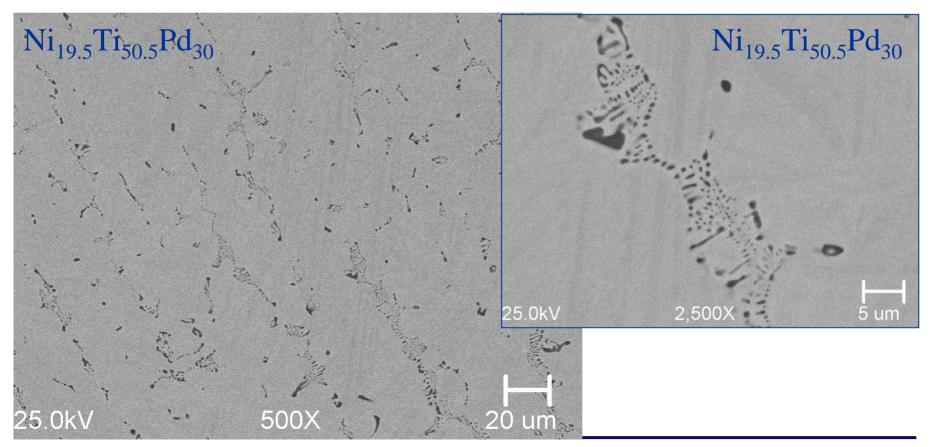
Materials Preparation

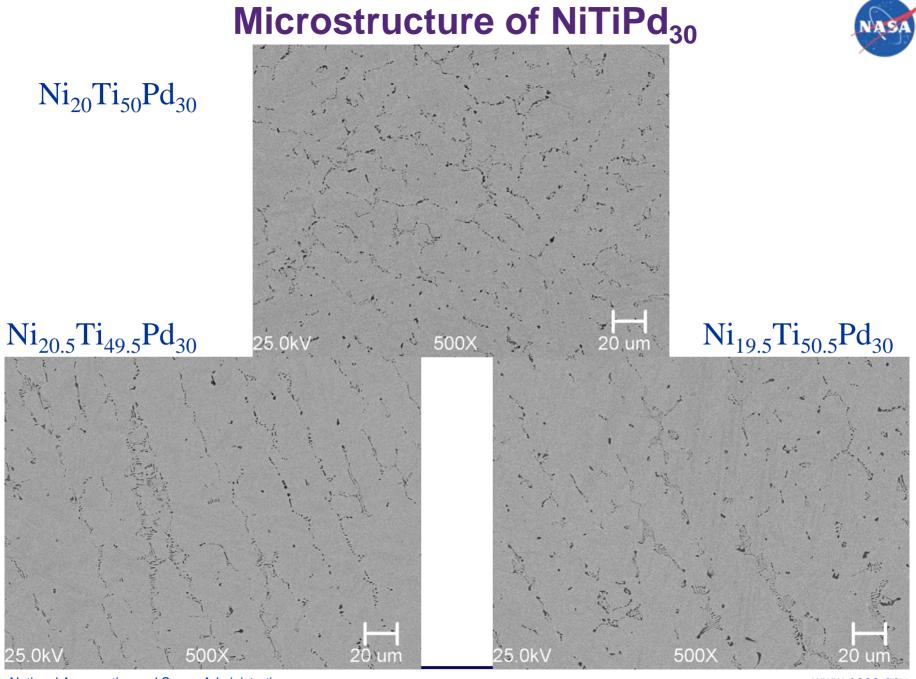
- Melted range of NiTiPdX (X=Au, Hf, Pt) alloys with equivalent Titanium (Ti+Hf) compositions ranging from 50.5 to 49 at%
 - Baseline: Ni₂₀Ti₅₀Pd₃₀
 - Au and Pt substitute for Pd -> Ni₂₀Ti₅₀Pd₂₅Au₅ and Ni₂₀Ti₅₀Pd₂₅Pt₅
 - Hf substitutes for Ti -> Ni₂₀Ti₄₇Pd₃₀Hf₃
- Vacuum arc melted 30g ingots & homogenized at 900C/72hrs
- 10mm long by 5mm diameter samples cut by wire EDM

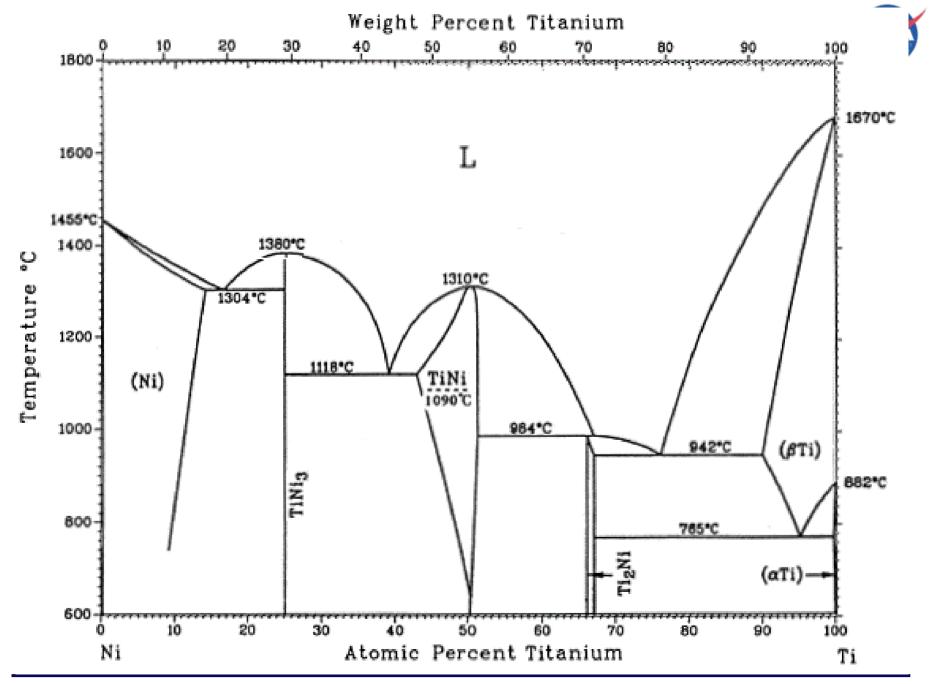
Microstructure of Ti-rich NiTiPd₃₀ @ 500X

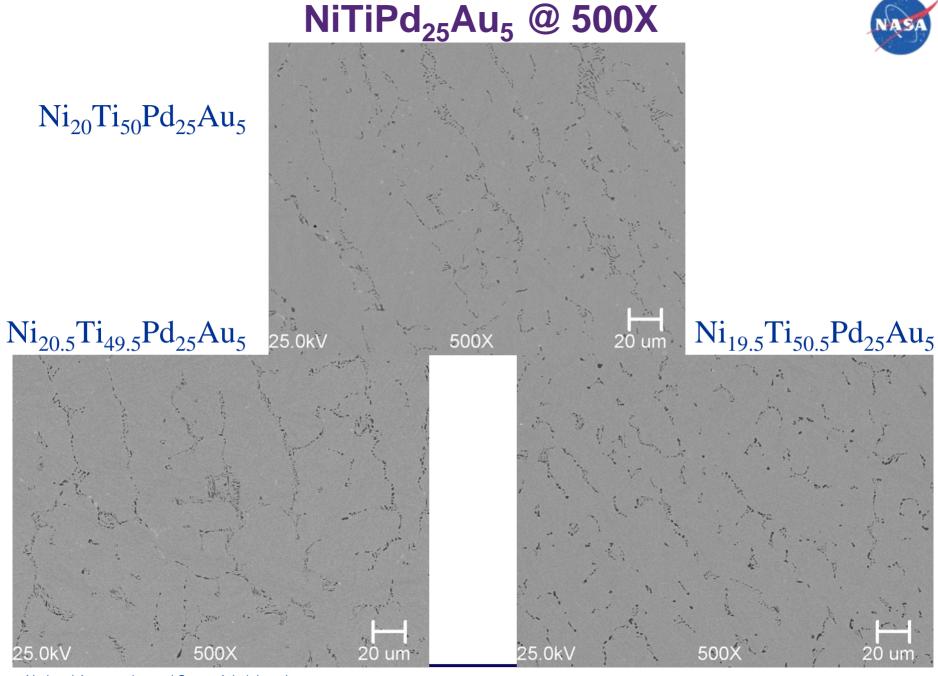


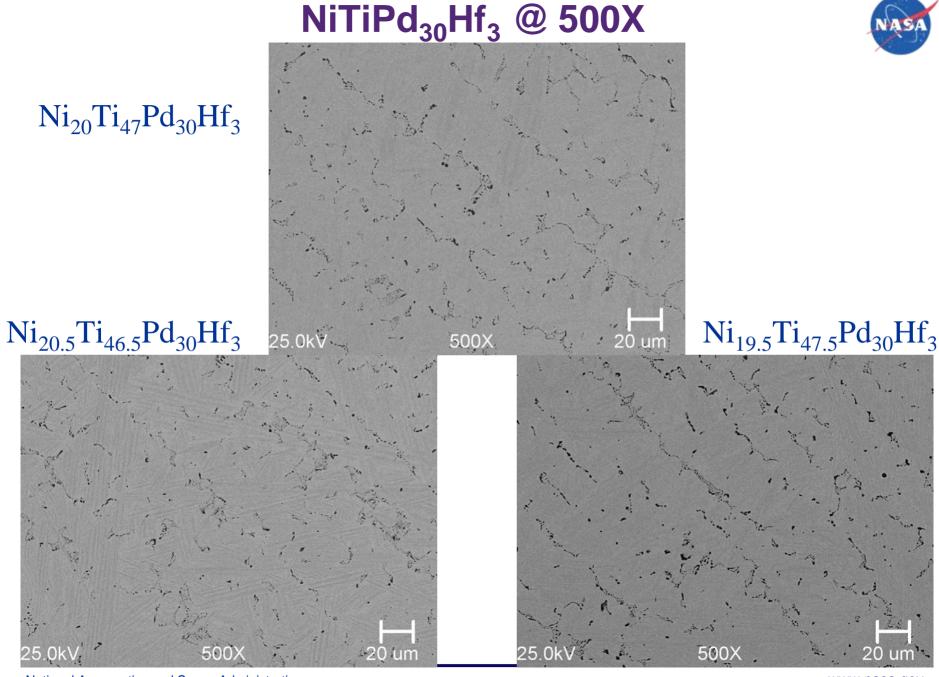
- Ti-rich microstructure shows expected Ti₂(Ni,Pd) phase in martensite matrix
- Interdendritic phase which forms during alloy solidification

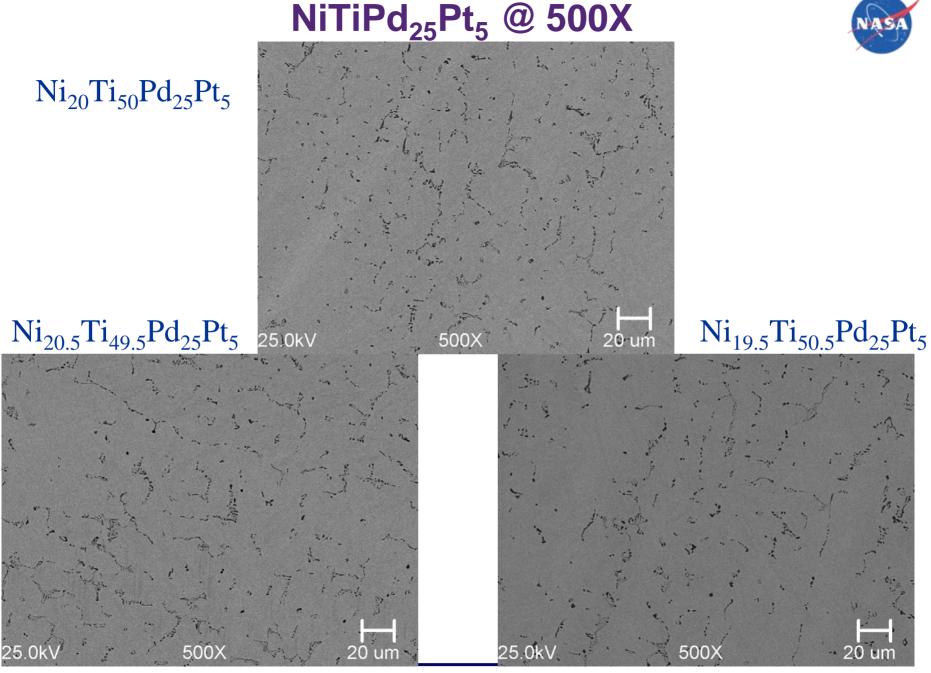








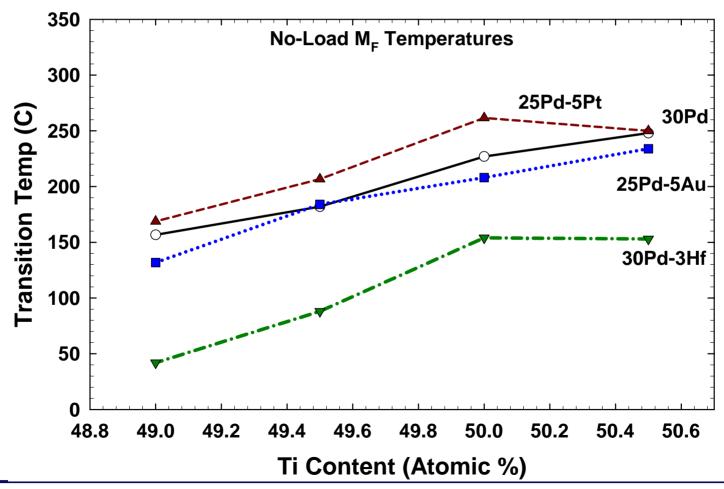






No-Load Martensite Finish Temperatures

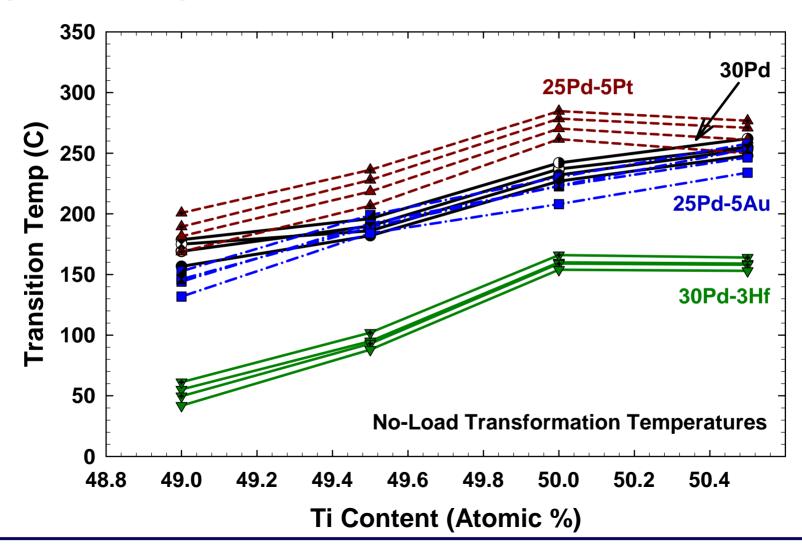
All alloys show characteristic drop in transformation temperature on Ti-lean side



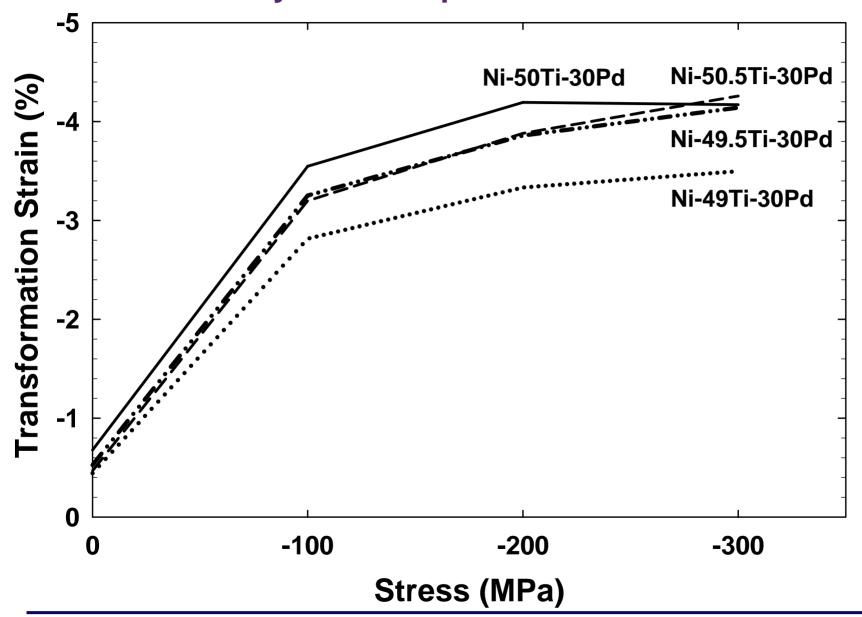
No-Load Transformation Temperature



 A_S , A_F , and M_S all parallel trend in M_F temperatures

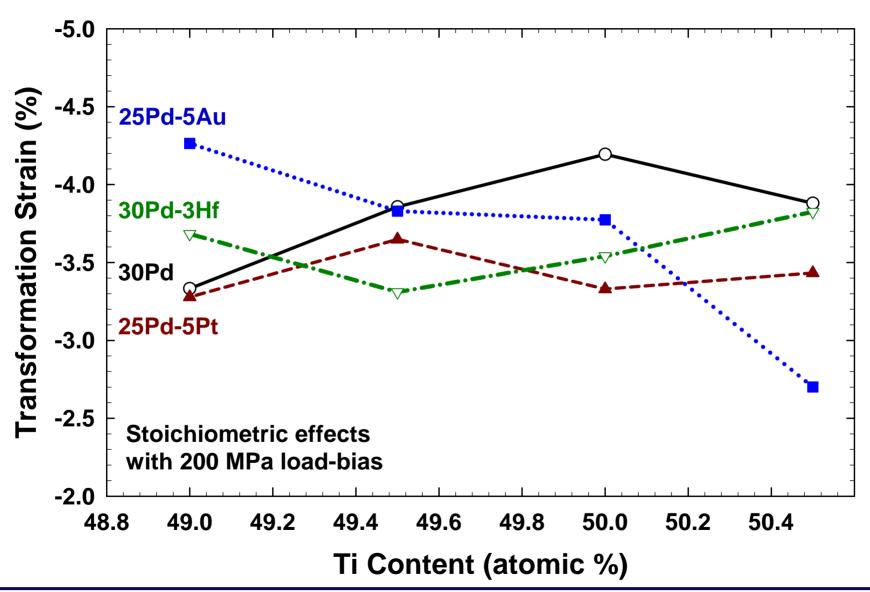


NiTiPd alloy - compositions on either side of stoichiometry see a dropoff in transformation strain



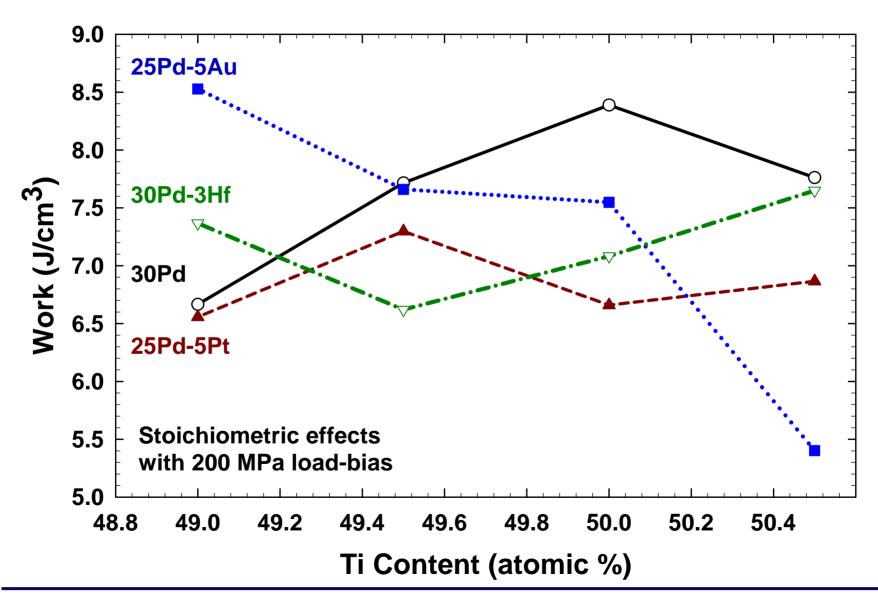
Transformation Strain – Drops slightly in quaternary alloys





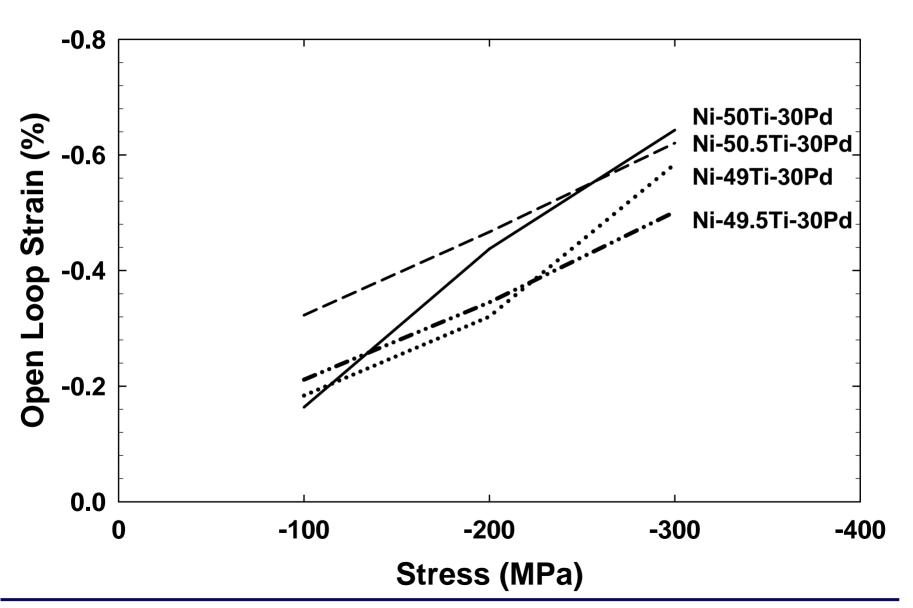
Work -Scaled value of transformation strain - ∫o dε





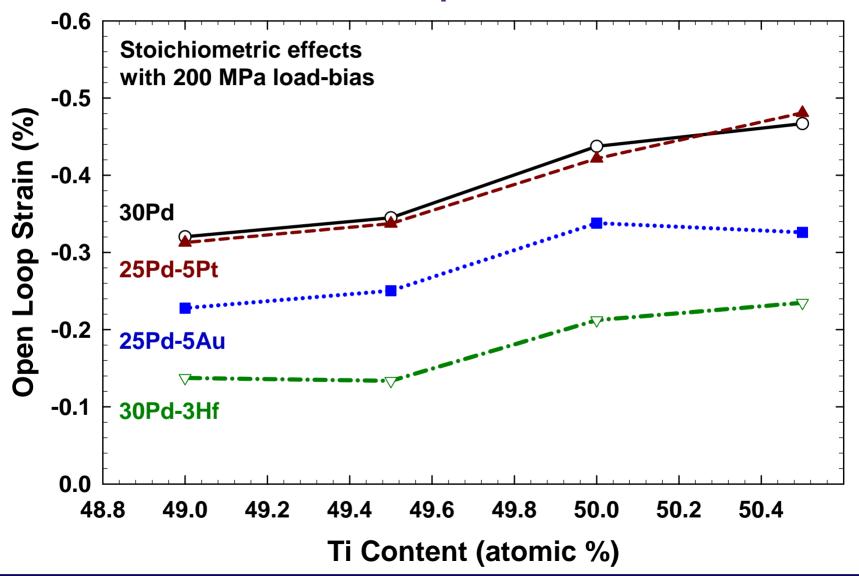
NiTiPd alloy – Open loop strain higher in Ti-rich than in Ti-lean





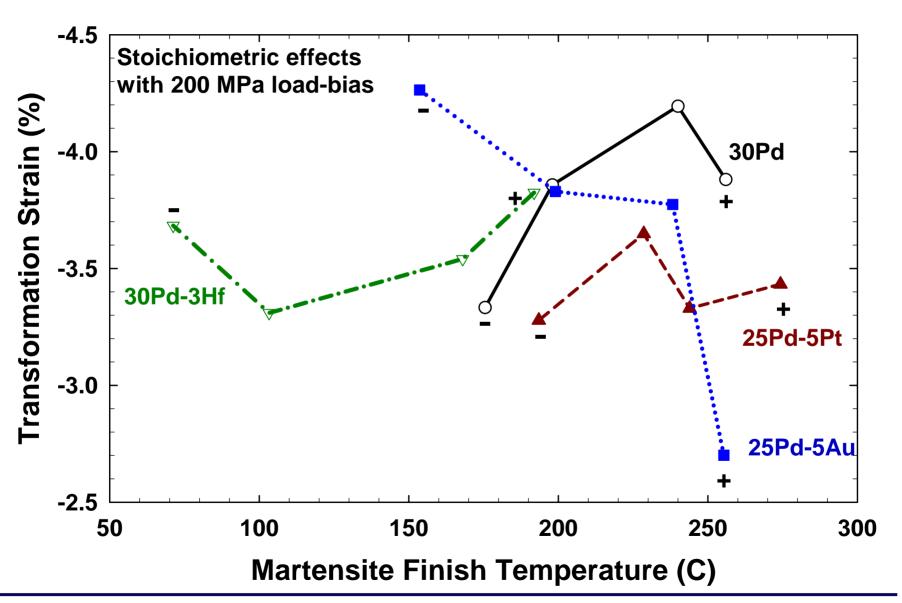
Open Loop Strain decreased by quaternary alloying, lowest in Tilean compositions





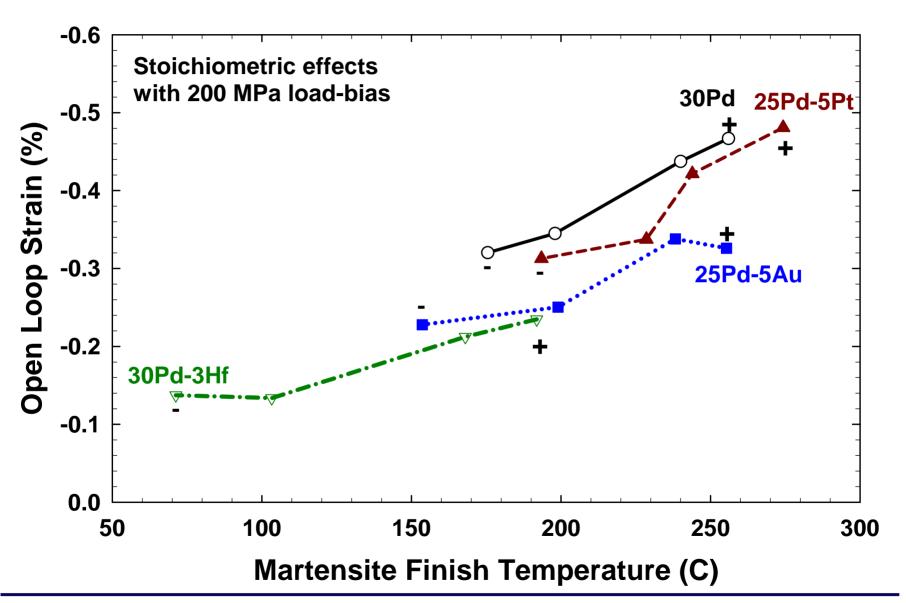
Transformation Strain -Decreased by quaternary additions





Open Loop Strain -Lowest in Ti-lean compositions at expense of Tf







Summary

- Quaternary alloying with Au, Pt, and Hf decrease transformation strain with respect to the baseline stoichiometric NiTi-30Pd alloy
- Ternary NiTiPd shows degradation of transformation strain with decreasing Ti content
- Hf and Pt alloys show relatively uniform transformation strains over the range of compositions
- Au alloyed material shows improvement in transformation strain with decreasing Ti composition
- Quaternary alloying with Au, Hf, and Pt reduced open loop strain
- Open loop strain also reduced in Ti-lean compositons over that of Ti-rich compositions



Conclusion

- If stability is not an issue, then ternary NiTiPd alloy, or Ti-rich NiTiPdX alloys are better for high transformation application (except Au)
- If stability is an issue, quaternary NiTiPdX alloys are better, with Hf showing greater benefit than Au or Pt and at lower levels, but with lower transformation temperature
 - Transformation temperature could be brought back up by reducing level of Hf



Questions?